

PTO 07-6227

CC=JP DATE=19960220 KIND=A
PN=08050922

ELECTRODE FOR CELL AND LITHIUM SECONDARY CELL EQUIPPED WITH THE ELECTRODE
[Denchiyo Denkyoku Oyobi Gai Denkyoku Wo Yu Suru Richiumu Niji Denchi]

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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. August 2007

Translated by: FLS, Inc.

PUBLISHING OFFICE	(19): JP
DOCUMENT NUMBER	(11): 08050922
DOCUMENT KIND	(12): A
PUBLICATION DATE	(43): 19960220
APPLICATION NUMBER	(21): 07128139
APPLICATION DATE	(22): 19950526
PRIORITY NUMBER	(31): 06116717
PRIORITY DATE	(32): 19940530
PRIORITY COUNTRY	(33): JP
INTERNATIONAL CLASSIFICATION	(51): H01M 10/38, 4/02, 4/62, 4/66, 10/40
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TITLE	(54): ELECTRODE FOR CELL AND LITHIUM SECONDARY CELL EQUIPPED WITH THE ELECTRODE
FOREIGN TITLE	[54A]: DENCHIYODENKYOKUOYOBIGAI DENKYOKU WO YU SURU RICHIMUMU NIJI DENCHI

[Claim 1] A lithium secondary cell having at least a negative electrode, separator, positive electrode and electrolyte or electrolytic solution; said lithium secondary cell characterized by the negative electrode having as components at least a metallic element which forms an alloy with lithium and a metallic element which does not form an alloy with lithium, and the output terminal on the negative electrode side being extracted from the metal part not forming an alloy with lithium.

[Claim 2] The lithium secondary cell of Claim 1 characterized by the content by percentage of the metallic element not forming an alloy with lithium being high in a part tied to a surface of the aforesaid negative electrode touching the electrolytic solution and facing the positive electrode, and to the output terminal.

[Claim 3] The lithium secondary cell of either one of Claims 1 and 2 characterized by the aforesaid negative electrode having a member containing a powdery metallic element which forms an alloy with lithium bound with a binder to a metal current-collecting member which does not form an alloy with lithium.

[Claim 4] The lithium secondary cell of any one of Claims 1 to 3 characterized by the aforesaid negative electrode being composed of an alloy of at least a metal which forms an alloy with lithium and a metal which does not form an alloy with lithium.

[Claim 5] The lithium secondary cell of any one of Claims 1 to 4 characterized by the member containing the aforesaid metallic element

* Numbers in the margin indicate pagination in the foreign text.

which forms an alloy with lithium comprising an alloy of at least two metals which are selectively etchable at different etching rates.

[Claim 6] The lithium secondary cell of any one of Claims 1 to 5 characterized by having, from out of the aforesaid negative electrodes, a negative electrode whose specific surface area was increased by selectively etching at least either side of the metallic element forming an alloy with lithium or the metallic element not forming an alloy with lithium.

[Claim 7] The lithium secondary cell of any one of Claims 1 to 6 characterized by a difference between one-half of a maximum height of the roughness (between highest peak and deepest valley) R_{max} of a conductor portion of the surface of the negative electrode touching the aforesaid electrolytic solution and facing the positive electrode, and the centerline average roughness R_a being at most one-tenth the distance between the surface of the negative electrode and the surface of the positive electrode.

[Claim 8] The lithium secondary cell of any one of Claims 1 to 7 characterized by $1 + (4nR_n/L)$ being at least 1.05, in relation to the roughness of the conductor portion on the aforesaid surface of the negative electrode when the centerline average roughness is defined as R_a , the measured length is defined as L , and the number of peaks per measured length L is defined as n .

[Claim 9] The lithium secondary cell of any one of Claims 1 to 8 characterized by providing a conductor layer, wherein the coefficient of extension is higher than that of the metal forming an alloy with lithium at room temperature, in the current-collecting portion of the aforesaid negative electrode.

[Claim 10] The lithium secondary cell of any one of Claims 1 to 6 characterized by the aforesaid metallic element forming an alloy with lithium being one or more elements selected from aluminum, magnesium, potassium, sodium, calcium, strontium, barium, silicon, germanium, tin, lead, indium and zinc.

[Claim 11] The lithium secondary cell of any one of Claims 1 to 6 characterized by the current-collecting member comprising the aforesaid metallic element not forming an alloy with lithium being one or more elements selected from nickel, titanium, copper, silver, gold, platinum, iron, cobalt, chromium, tungsten and molybdenum.

[Claim 12] The lithium secondary cell of Claim 9 characterized by the conductor layer, which has a coefficient of extension and arranged in the aforesaid current-collecting portion of the negative electrode, being composed of one or more kinds of conductors selected from tin, a tin-bismuth alloy, a tin-lead alloy, a zinc-aluminum alloy, a copper-zinc alloy or a cadmium-zinc alloy, and a conductive ink in which conductor fine particles are bound with an organic polymer material.

[Claim 13] The lithium secondary cell of Claim 12 characterized by the organic polymer in the conductive ink used for the conductor layer having a high coefficient of extension of the aforesaid negative electrode current-collecting portion being a fluorine resin which does not react with the electrolytic solution, a polyolefin, a silicone resin or a highly-crosslinked polymer.

[Claim 14] The lithium secondary cell of Claim 1 characterized by the positive electrode-activating material, which constitutes the aforesaid

positive electrode, containing elemental lithium.

[Claim 15] The lithium secondary cell of any one of Claims 1 to 8 characterized by the aforesaid negative electrode surface being covered with an insulator film or semiconductor film which is not dissolved by the electrolytic solution and is capable of allowing lithium ions to penetrate therethrough but does not allow deposited lithium metal to penetrate therethrough.

[Claim 16] An electrode for a cell characterized by having as components a metallic element forming an alloy with lithium and a metallic element not forming an alloy with lithium, and an output terminal being extracted from the metal part which does not form an alloy with lithium.

[Claim 17] The electrode for a cell of Claim 16 characterized by the content by percentage of the metallic element not forming an alloy with lithium being high in the part tied to a surface of the aforesaid negative electrode touching the electrolytic solution and facing the positive electrode, and to the output terminal.

[Claim 18] The electrode for a cell of Claim 16 or 17 characterized by the aforesaid negative electrode having a member containing a powdery metallic element which forms an alloy with lithium bound to a metal current-collecting member which does not form an alloy with lithium with a binder.

[Claim 19] The electrode for a cell of Claims 16 to 18 characterized by the aforesaid negative electrode being composed of an alloy of at least a metal which forms an alloy with lithium and a metal which does not form an alloy with lithium.

[Claim 20] The electrode for a cell of Claims 16 to 19 characterized by the member containing the aforesaid metallic element which forms an alloy with lithium comprising an alloy of at least two metals which are selectively etchable at different etching rates.

[Claim 21] The electrode for a cell of Claims 16 to 20 characterized by having, from out of the aforesaid negative electrodes, a negative electrode whose specific surface area was increased by selectively etching at /3 least either side of the metallic element forming an alloy with lithium or the metallic element not forming an alloy with lithium.

[Claim 22] The electrode for a cell of Claims 16 to 21 characterized by a difference between one-half of a maximum height of the roughness (between highest peak and deepest valley) R_{max} of a conductor portion of the surface of the negative electrode touching the aforesaid electrolytic solution and facing the positive electrode, and the centerline average roughness R_a being at most one-tenth the distance between the surface of the negative electrode and the surface of the positive electrode.

[Claim 23] The electrode for a cell of Claims 16 to 22 characterized by $1 + (4nR_a/L)$ being at least 1.05, in relation to the roughness of the conductor portion on the aforesaid surface of the negative electrode when the centerline average roughness is defined as R_a , the measured length is defined as L , and the number of peaks per measured length L is defined as n .

[Claim 24] The electrode for a cell of Claims 16 to 23 characterized by providing a conductor layer, wherein the coefficient of extension is higher than that of the metal forming an alloy with lithium at room temperature, in the current-collecting portion of the aforesaid negative electrode.

[Claim 25] The electrode for a cell of Claims 16 to 21 characterized by the aforesaid metallic element forming an alloy with lithium being one or more elements selected from aluminum, magnesium, potassium, sodium, calcium, strontium, barium, silicon, germanium, tin, lead, indium and zinc.

[Claim 26] The electrode for a cell of Claims 16 to 21 characterized by the current-collecting member comprising the aforesaid metallic element not forming an alloy with lithium being one or more elements selected from nickel, titanium, copper, silver, gold, platinum, iron, cobalt, chromium, tungsten and molybdenum.

[Claim 27] The electrode for a cell of Claim 24 characterized by the conductor layer, which has a coefficient of extension and arranged in the aforesaid current-collecting portion of the negative electrode, being composed of one or more kinds of conductors selected from tin, a tin-bismuth alloy, a tin-lead alloy, a zinc-aluminum alloy, a copper-zinc alloy or a cadmium-zinc alloy, and a conductive ink in the conductor fine particles are bound with an organic polymer material.

[Claim 28] The electrode for a cell of Claim 27 characterized by the organic polymer in the conductive ink used for the conductor layer having a high coefficient of extension of the aforesaid negative electrode current-collecting portion being a fluorine resin which does not react with the electrolytic solution, a polyolefin, a silicone resin or a highly-crosslinked polymer.

[Claim 29] The electrode for a cell of Claim 6 characterized by the positive electrode-activating material, which constitutes the aforesaid

positive electrode, containing elemental lithium.

[Claim 30] The electrode for a cell of Claims 16 to 23 characterized by the aforesaid negative electrode surface being covered with an insulator film or semiconductor film which is not dissolved by the electrolytic solution and is capable of allowing lithium ions to penetrate therethrough but does not allow deposited lithium metal to penetrate therethrough.

[Detailed Specifications]

[0001]

[Field of Industrial Application] The present invention relates to a lithium secondary cell which uses lithium as the negative electrode, and in particular, a lithium secondary cell capable of suppressing the occurrence of lithium dendrites (resinous protrusions) generated by repeated charging/discharging, and capable of suppressing a reduction in the current-collecting ability.

[0002]

[Prior Art] The possibility of global warming occurring in recent years has been pointed out due to the greenhouse effect owing to an increase in CO₂ contained in the atmosphere. Although heat energy obtained by burning fossil fuels is converted to electrical energy at thermal power stations, the equipment has become complex for new thermal power stations because of these CO₂ emissions following burning. Therefore, performing a so-called load leveling for standardizing a load by accumulating power at night, which is surplus power, in secondary cells installed in common households as an effective utilization of a power generator is being advocated. In addition, developing lightweight, high energy density secondary cells

for electric cars which do not emit substances said to be related to air pollution and containing COx, NOx, SOx, hydrocarbons, and the like, and developing small, lightweight and high-performance secondary cells used in the power supplies of portable equipment, such as book-type personal computers, word processors, video cameras and portable telephones have been increasingly demanded.

[0003]

[Problems to be Solved by the Invention] Development of a rocking chair-type lithium ion cell using lithium ions that have been introduced into an intercalation compound as the positive electrode-activating material and carbon as the negative electrode-activating material is progressing and is partly being put to practical use as the high-performance secondary cell mentioned above. However, lithium secondary cells currently on hand have not achieved enough high energy density, which is an original feature of lithium cells using metallic lithium as the negative electrode-activating material. It cannot be said that high-capacity lithium batteries using a lithium metal noteworthy as a negative electrode have not been put to practice sufficiently as high-energy-density secondary cells. Dendritic lithium may deposit on the negative electrode of a lithium secondary cell during charging. This phenomenon may be a cause of short circuits and self-discharging. One of the reasons a high-capacity lithium battery (secondary cell) cannot be put to practical use sufficiently is because the generation of lithium dendrites, which are the main cause of short circuits generated by repeated charging/discharging, has not been successfully checked. If a lithium dendrite grows and the negative and

positive electrodes are short circuited, the energy of the cell is consumed in a short time at that part; hence, the cell generates heat, the solvent of the electrolytic solution is decomposed by the heat or the like to generate a gas, and the internal pressure of the cell may increase. In either case, dendritic growth is readily tied to damage of a cell and a reduced lifespan owing to short circuits.

[0004] In addition, a method in which a lithium alloy, such as lithium-aluminum, is used for the negative electrode also has been attempted to suppress the reactivity of the lithium as well as the generation of dendrites. However, even if generation of dendrites can be suppressed, at the present time, no secondary cells having a high energy density /4 or a long enough cycle life have been put to practical use yet.

[0005] An example in which a lithium alloy is used as the negative electrode is indicated in the publications of, e. g., Tokkai Nos. 63-13264, 5-47381, 5-190171, etc. However, even if a lithium alloy was used as the negative electrode, there were cases, during repeated charging/discharging, in which the negative electrode repeatedly expanded and contracted, cracks and so forth developed in the negative electrode, and sufficient current collection properties could not be maintained.

[0006] In addition, in the publication of Tokkai No. 63-114057 is indicated a negative electrode using a mixed sintered body comprising fibrous aluminum and metal fibers which are not alloyed with lithium as the base. However, in this case, a reduction in the binding strength with the metal fibers that are not alloyed with lithium owing to expansion and contraction of fibrous aluminum due to charging and discharging and

cracks in the interface therewith occur, so a sufficient current collection property may not be maintained.

[0007] Furthermore, in the publication of Tokkai No. 5-234585 is disclosed a cell wherein a metal powder, which hardly generates an intermetallic compound with lithium metal, sticks evenly to the surface of the base material comprising lithium metal, hardly any dendrites are deposited, the charging efficiency is increased, and the cycle life is improved. However, as a result of repeated expansion and contraction of the lithium metal base material and exfoliation of stuck powder and occurrence of cracks in the base material, the maintenance of a sufficient current collection property by the negative electrode and the suppression of the deposition of dendrites, as described above, still may not be sufficient.

[0008] In addition, a lithium secondary cell using aluminum foil whose surface was etched as the negative electrode is reported in the Journal of Applied Electrochemistry 22 (1992): 620-627. However, as a result of the repeated expansion and contraction of the aluminum foil due to a repeated charging/discharging by repeating the charge/discharge cycle to a practical level, fissures develop in the aluminum foil and cause a reducing in the current collection property and dendritic growth. Consequently, in this case, a cell having a long cycle life at a practical level is not obtained. Such being the case, whereas the advent of a negative electrode and a lithium secondary cell having a high energy density and a long cycle life is awaited and desired, the fact of the matter, however, is that problems still have to be solved.

[0009] (Purpose of the Invention) It is an object of the present

invention to provide a lithium secondary cell capable of solving the aforementioned problems, and has a long cycle life and high energy density.

[0010] It is another object of the present invention to provide a lithium secondary cell having an electrode for a cell having a negative electrode structure capable of checking a reduction in the current collecting ability due to the lithium being made a fine powder by deposition and dissolution thereof during charging/discharging and the development of fissures.

[0011]

[Means for Solving the Problems and Effects] The electrode for a cell of the present invention which solves the above-mentioned problems and achieves the above-mentioned object is characterized by the negative electrode having as components at least a metallic element which forms an alloy with lithium and a metallic element which does not form an alloy with lithium, and the output terminal being extracted from the metal part not forming an alloy with lithium.

[0012] In addition, the lithium secondary cell of the present invention is a lithium secondary cell having at least a negative electrode, separator, positive electrode and electrolyte or electrolytic solution; said lithium secondary cell characterized by the negative electrode having as components at least a metallic element which forms an alloy with lithium and a metallic element which does not form an alloy with lithium, and the output terminal on the negative electrode side being extracted from the metal part not forming an alloy with lithium.

[0013] This is based on the fact that, as a result of repeated painstaking

research to solve the above-mentioned problems, an inventor of the present invention discovered that a lithium secondary cell having a long life wherein the generation of lithium dendrites is checked was obtained by suitable using a negative electrode compounded from a metal alloyed with lithium and a metal not alloyed with lithium.

[0014] That is, the above-mentioned problems can be solved by means of a lithium secondary cell having at least a negative electrode, separator, positive electrode, electrolyte or electrolytic solution, and a cell case; said lithium secondary cell characterized by the negative electrode being composed of at least a metallic element which forms an alloy with lithium and a metallic element which does not form an alloy with lithium, and the output terminal on the negative electrode side being extracted from the metal not forming an alloy with lithium. By arranging the metal not forming an alloy with lithium in the current-collecting portion of the negative electrode as such, making the lithium a fine powder owing to deposition and dissolution thereof at the time of charging/discharging, the generation of fissures, and a decline in the current collecting ability can be checked.

[0015] Furthermore, it is preferable to increase the content by percentage of the metallic element not forming an alloy with lithium in a current-collecting part tied to a surface of the negative electrode touching the electrolytic solution and facing the positive electrode, and to the output terminal.

[0016] With the negative electrode comprising an element forming an alloy with lithium, at the time of charging the lithium deposits, is

alloyed, and expands, and at the time of discharging, the lithium is released into the electrolytic solution, contracts and fine powdering arises. This fine powdering arises the most actively on the surface of the negative electrode where the element forming an alloy with lithium is present. The conductivity decreases and the current collecting ability decreases markedly where the fine powdering arose. As a consequence, by enhancing the content by percentage of the metallic element not forming an alloy with lithium on the surface of the conductive part of the negative electrode touching the electrolytic solution and facing the positive electrode, the conductivity is maintained via the metal not forming an alloy with lithium at the time of fine powdering as well; hence, a reduction in the current collecting ability can be suppressed more.

[0017] Moreover, the negative electrode of the present invention can be formed by binding with a binder a powdery member containing a metallic element which forms an alloy with lithium to a metal current-collecting member of a metal which does not form an alloy with lithium.

[0018] By making such a negative electrode, fatigue fracture arising from repeated expansion due to alloying with lithium at the time of charge, and contraction due to elution of lithium at the time of discharge can be suppressed. In addition, by adopting a powder, the specific surface /5 area of the negative electrode can be increased, the contact area with the electrolytic solution increases, and diffusion of lithium ions into the negative electrode can be facilitated. Furthermore, by conducting a treatment, such as etching, the specific surface area can be increased further, lithium dendrite growth can be checked and the charging and

discharging efficiency can be increased. Moreover, suppressing the thickness of the negative electrode and the concentration of the metallic element forming an alloy with lithium and the metallic element not forming an alloy with lithium in the negative electrode becomes easy.

[0019] When the member containing the metallic element forming an alloy with lithium in the negative electrode is grown and not sintered, it is necessary to mix about 1 to 25% by weight of a conduction adjuvant such as a carbon powder or metal powder and enhance the current collectibility of the powders of the member containing the metallic element not forming an alloy with lithium. The impedance of the electrode decreases easily since the electrolytic solution easily has a lower bulk density for the above-mentioned conduction adjuvant. The bulk density of the conduction adjuvant is more preferably at most 0.1.

[0020] In addition, the finer the particle size of the conduction adjuvant is the better it is, and to increase the current collectibility by increasing the packing density, conduction adjuvants having shapes, such as spherical, needle and flaky, should be combined.

[0021] When it is sintered, the material used in the binder is an inorganic or organic material which does not release to the best of its ability a corrosive gas, such as a halogen gas, under high temperatures, and in the case of an organic material, a readily-carbonized polymer is preferable. The sintering atmosphere is preferably under reduced pressure, under an inert gas or under a reducing gas.

[0022] Still further, an alloy of at least a metal forming an alloy with lithium and a metal not forming an alloy with lithium can further

be used for the negative electrode of the present invention. Thus, the current collecting ability can be increased as far as the inside of the negative electrode, and the charging/discharging cycle life can be extended further.

[0023] Also, the member of the negative electrode containing the metallic element forming an alloy with lithium may comprise an alloy of at least two metals selectively etchable at different etching rates. By further conducting an etching treatment on this negative electrode, the specific surface area of the negative electrode can be increased rapidly.

[0024] It also is preferable to increase the specific surface area of the negative electrode by selectively etching the metallic element forming an alloy with lithium or the metallic element not forming an alloy with lithium. By increasing the specific surface area of the negative electrode, the reactivity of the surface of the negative electrode is enhanced and the essential current density is reduced, the charging/discharging reaction is carried out smoothly, and as a result, the cycle life can be extended.

[0025] When protruding portions are present on the negative electrode surface in order to increase the specific surface area by providing it with an uneven shape, at the protruding portions, the electric field becomes concentrated at the time of charging and the current density increases; hence, the lithium dendritic growth occurs readily to easily become the cause of short circuits.

[0026] Therefore, the difference between one-half of a maximum height of the roughness (between highest peak and deepest valley) R_{max} of a conductor

portion of the surface of the negative electrode touching the aforesaid electrolytic solution and facing the positive electrode, and the centerline average roughness being at most one-tenth the distance between the surface of the negative electrode and the surface of the positive electrode.

[0027] In addition, it is preferable that the ratio of the electric conductivity of the valley portions on the surface of the negative electrode to the conductivity of the protruding portions thereon be set to at most 10. That is, even when the difference between one-half of a maximum height of the roughness R_{max} of a conductor portion of the surface of the negative electrode is larger than one-tenth the distance between the negative and positive electrode surfaces, and when the electrical resistance of the protruding portions is larger than that of the flat portions, the line of electrical power is not concentrated in the protruding portions and the field strength does not increase; hence, there is no dendritic growth of lithium in the protruding portions at the time of charging.

[0028] When the conductivity of the conductor portion on the surface of the negative electrode was uniform or substantially uniform, the maximum height R_{max} and centerline average roughness R_a were measured, as shown in Figure 6 on the surface of the negative electrode before assembling the cell in a tracer method, the cycle life of various negative electrodes was measured at conditions where dendritic growth of lithium, which formed a cell using that negative electrode and enhanced the charging voltage occurred easily, and these measurements were correlated. As a result, a correlation to a certain degree was found, as shown in Figure 7, between the cycle life of the negative electrode and the difference between one-half

of a maximum height of the roughness (between highest peak and deepest valley) R_{max} of a conductor portion of the surface of the negative electrode corresponding to the positive electrode and the centerline average roughness R_a being at most one-tenth the distance between the surface of the negative electrode and the surface of the positive electrode. In short, when the difference between one-half the value obtained by subtracting the minimum height from the maximum height of the roughness of the conductor portions on the surface of the negative electrode and the centerline average roughness was set to at most one-tenth the distance between the negative and positive electrode surfaces, it was proven that the cycle life could be extended further.

[0029] Moreover, it is preferable that $1 + (4nR_a/L)$ be at least 1.05, in relation to the roughness of the conductor portion on the aforesaid surface of the negative electrode of the present invention when the centerline average roughness is defined as R_a , the measured length is defined as L , and the number of peaks per measured length L is defined as n .

[0030] As a result of more painstaking investigations, it was seen that by roughening the surface of the negative electrode by an etching treatment and the like, the reactivity of the surface increased, the specific surface area increased, the essential current density decreased, and the charging/discharging cycle life could be extended. It was seen that it was preferable that $1 + (4nR_a/L)$ be at least 1.05, preferably, at least 1.1, and more preferably, at most 1.2 when the data as shown in Figure 8 was obtained, and the centerline average roughness was defined as R_a , the measured length was defined as L , and the number of peaks per measured

length L was defined as n; hence, the cycle life was extended two-fold or more. Moreover, the results upon measuring the charging/discharging cycle life are shown in Figure 8 by using aluminum as the element forming an alloy with the lithium of the negative electrode of the present invention, roughening the surface with various etching treatments, subsequently, using an electrolytic solution obtained by dissolving lithium borofluoride in a mixed solvent of ethylene carbonate dimethyl carbonate (EC-DMC) or propylene carbonate diethyl carbonate (PC-DEC) as the electrolytic solution, and assembling the cell.

[0031] In the present invention, a conductor layer having a higher coefficient of extension at room temperature higher than the metal forming an alloy with lithium may be provided in the conductor portion of /6 the negative electrode. When a lithium-aluminum alloy foil or aluminum foil is used for the negative electrode, fine powdering arises on the surface of the negative electrode by repeated charging/discharging, fissures develop therein, and current collection becomes impossible in the end. It is surmised this is the primary factor of expansion and contraction of the negative electrode at the time of charging/discharging. However, by providing a conductor layer having a high coefficient of extension at room temperature in the current collection portion, fissures in the current collection portion caused by expansion and contraction of the negative electrode are further checked, and a current collection ability can be ensured.

[0032] Elemental lithium may be contained in the positive electrode-activating material constituting the positive electrode. Thus,

deposition of the lithium at the time of charging is performed first, then alloying of the element forming an alloy with the lithium in the negative electrode is performed. After the cell is assembled, the lithium alloy is not fabricated or prepared in advance; hence, the manufacturing process is simplified. In addition, since the lithium present in the positive electrode is released and inserted before charging/discharging; hence, expansion and contraction of the positive electrode following discharging and charging is lessened, and exfoliation of the positive electrode-activating material from the current collector does not occur; hence, the cycle life is extended.

[0033] Still further, the lithium ions penetrate through the surface of the negative electrode, but they are deposited at the time of charging and the lithium metal does not penetrate therethrough. Thus, it is difficult for the lithium deposited during charging to come in contact directly with the electrolytic solution, and the reactants that the active lithium reacts with and cannot participate in discharging are prevented from being produced, while the charging/discharging cycle life can be extended. Next, when the negative electrode is formed from a powder, there is an effect of checking exfoliation of the powder as well.

[0034] The lithium secondary cell of the present invention will now be described with reference to the drawings.

[0035] A cross-sectional schematic diagram of an example of a negative electrode capable of being used ideally in the lithium secondary cell of the present invention was shown in each of Figures 2 and 3, respectively. Moreover, although not shown, a case in which it actually constitutes

the cell is provided in which a separator and positive electrode face the upper part of the illustrated negative electrodes in Figures 2 and 3.

[0036] The negative electrode shown in Figure 2(a) is a case of a negative electrode composed of a member 102 containing a metallic element not forming an alloy with lithium and a current-collecting portion 101 comprising a metallic element forming an alloy with lithium. The negative electrode shown in Figure 2(a) expands as the lithium ions in the electrolytic solution are alloyed with the member 102 containing the metallic element forming an alloy with lithium and are deposited during charging. Then, at discharge, it contracts as the lithium ions are released from the member 102 containing the metallic element forming an alloy with lithium into the electrolytic solution. Due to expansion and contraction due to this charging/discharging, finer powdering of the member 102 containing the metallic element forming an alloy with lithium and fissures occur, but the current-collecting portion 101 not forming an alloy with lithium is provided in the current collection portion; hence, a reduction in the current collection ability is lessened, and exfoliation of the fine powdered, fissured member 102 containing the metallic element forming an alloy with lithium into the electrolytic solution is checked.

[0037] The negative electrode shown in Figure 2(b) is a case in which a metallic element 106 not forming an alloy with lithium is arranged on the surface of the negative electrode having the configuration in Figure 2(a). In this case, a reducing on the current collection ability in the radial direction on the surface and fostering of fine powdering can be

checked on the surface of the negative electrode where fine powdering most readily occurs by the metallic element 106 not forming an alloy with lithium arranged on the surface of the negative electrode than in the case of the negative electrode having the configuration shown in Figure 2(a).

[0038] The negative electrode shown in Figure 2(c) is bound to the current-collecting portion 101 comprising a metallic element not forming an alloy with lithium with a binder 105 by mixing a conduction adjuvant 104 with a powdery member 103 containing a metallic element forming an alloy with lithium to form an active layer. By using the powder from the start without using a bulky member for the one containing the metallic element forming an alloy with lithium, stress owing to expansion and contraction generated during charging/discharging can be alleviated, fatigue fracture is prevented, and the charging/discharging cycle life can be further extended. In addition, the contact area with the electrolytic solution can be increased and the reaction during charging/discharging can be performed more smoothly.

[0039] The negative electrode shown in Figure 2(c') forms a similar active layer as the negative electrode shown in Figure 2(c) on both sides of the current-collecting portion 101 comprising a metallic element not forming an alloy with lithium. In this case, the separator and positive electrode may be arranged opposite the upper and lower parts. The electrode configuration of the negative electrode shown in Figure 2(c') having an active layer provided on both sides with a current collection portion in common is more effective from the standpoint of curtailing the

manufacturing process and material and increasing the electrical capacity per unit volume especially for a spiral cylindrical cell or a square cell having a laminated-type electrode shape.

[0040] The negative electrode shown in Figure 3(d) is a negative electrode obtained by providing a conductor layer 107 having a high coefficient of extension between the member 102 containing the metallic element forming an alloy with lithium and the current-collecting portion 101 comprising the metallic element not forming an alloy with lithium having the configuration in Figure 1(a). When fissures occur in the member 102 containing the metallic element forming an alloy with lithium due to expansion and contraction due to the charging/discharging cycle, following the conductor layer 107 having a high coefficient of extension during expansion and contraction, it can check a reduction in the current collection ability better. In addition, exfoliation of the member 102 containing the metallic element forming an alloy with lithium into the electrolytic solution also can be prevented.

[0041] The negative electrode shown in Figure 3(e) is a negative electrode has a metallic element 106 not forming an alloy with lithium arranged on the front and back of the member 102 containing the metallic element forming an alloy with lithium, and the current collection portion is covered with a conductor layer 107 having a high coefficient of extension. The problems of the surface of the negative electrode owing to repeated charging/discharging cycle, i.e., a reduction in the current collection ability of the current collection portion and exfoliation of the member 102 containing the metallic element forming an alloy with lithium into

the electrolytic solution also can be prevented.

[0042] The negative electrode shown in Figure 3(f) is an example in which the current collection portion having the configuration shown in Figure 3(a) is covered with the conductor layer 107 having a high coefficient of extension. It can check a reduction in the current collection ability of the current collection portion and also prevent exfoliation of the member 102 containing the metallic element forming an alloy with lithium into the electrolytic solution.

[0043] The negative electrode shown in Figure 3(g) employed an alloy 108 of the metallic element forming an alloy with lithium and the 17 metallic element not forming an alloy with lithium. It also can be applied to a case in which the member containing the metallic element forming an alloy with lithium is a powder, as in the case of the negative electrode shown in Figure 3(c). By using the alloy 108 of the metallic element forming an alloy with lithium and the metallic element not forming an alloy with lithium, the metallic element not forming an alloy with lithium is arranged as far as the fine part inside, and the current collection ability can be maintained, while fine powdering of the metal forming an alloy with lithium and generation of fissures can be prevented. Here, the proportion of the above-mentioned metallic element forming an alloy with lithium is favorably at least 50% so that the efficiency for utilizing lithium is not lowered. In addition, if the etching rates of the metallic element forming an alloy with lithium and the metallic element not forming an alloy with lithium differ, selective etching is possible. By etching and removing a portion of the metallic element forming an alloy with lithium

or the metallic element not forming an alloy with lithium, an extremely large specific surface area can be obtained.

[0044] By using the negative electrodes, as shown in Figures 2 and 3, and combining the positive electrode, separator and electrolyte, a secondary cell can be formed as shown in Figure 1. In Figure 1, 200 is a current collection portion comprising the metallic element not forming an alloy with lithium primarily; 201 is a layer comprising a member containing the metallic element forming an alloy with lithium; 202 is a negative electrode; 203 is a positive electrode; 204 is an electrolyte (electrolytic solution); 205 is separator; 206 is a negative electrode terminal; 207 is a negative electrode terminal; and 208 is a cell case. Moreover, it goes without saying that the configuration of the negative electrode 202 can be replaced respectively by the configurations of the negative electrodes shown respectively in Figures 2 and 3.

[0045] Since the negative electrode of the present invention is composed of the member containing the metallic element forming an alloy with lithium and the current collection portion comprising the metallic element not forming an alloy with lithium, even with repeated corrosion resistance, the current collection member comprising the metallic element not forming an alloy with lithium does not degrade, the current collection ability may be maintained, an elevation in the discharge voltage during a constant current discharge is checked, the generation of dendrites may be suppressed, and the cycle life can be extended as a result.

[0046] (Negative electrode) The negative electrode of the present invention has as components at least a metallic element forming an alloy

with lithium and a metallic element not forming an alloy with lithium, and the output terminal on the negative electrode side is extracted from the current collection portion in which the metal not forming an alloy with lithium was arranged.

[0047] For an actual negative electrode, a metallic element not forming an alloy with lithium that is arranged in the current collection portion of the platy or foil-like member containing the metallic element forming an alloy with lithium, or a layer comprising a powder containing the metallic element forming an alloy with lithium that is formed on a current collection member of a metal not forming an alloy with lithium is used. Furthermore, a metallic element not forming an alloy with lithium is arranged on the surface facing the positive electrode of the above-mentioned negative electrode to enhance the current collection ability.

[0048] An alloy of the metallic element forming an alloy with lithium and the metallic element not forming an alloy with lithium also can be used for the member containing the above-mentioned metallic element forming an alloy with lithium.

[0049] Furthermore, by covering the above-mentioned current collection portion of the negative electrode with the metal forming an alloy with lithium at room temperature at a conductive layer having a high coefficient of extension, fatigue fracture following expansion and contraction by repeated corrosion resistance is prevented.

[0050] <Arrangement of metallic element not forming an alloy with lithium> An example of a method in which the member comprising the metallic element forming an alloy with lithium is used as the negative electrode

base material, a treatment is conducted thereon, and the metallic element not forming an alloy with lithium is arranged will be described first. There is the method below for the method for arranging the above-mentioned metallic element not forming an alloy with lithium in the current collection portion with the surface facing the positive electrode of the negative electrode.

[0051] When the tendency for the metallic element forming an alloy with lithium to ionize is higher than that of the metallic element not forming an alloy with lithium, by immersing the member comprising the metallic element forming an alloy with lithium in a solution of a salt of the metallic element not forming an alloy with lithium, a portion of the metallic element forming an alloy with lithium can be substituted with the metallic element not forming an alloy with lithium. The amount of substitution can be controlled depending on the time of immersion in the solution, the concentration of the salt in the solution, the temperature of the solution, etc. That is, the amount substituted increases if the immersion time in the solution is lengthened, and the substitution reaction is increased if the concentration of the salt in the solution is increased or the temperature of the solution is increased.

[0052] For another method of arrangement, a method in which a base material is covered a layer containing the metallic element not forming an alloy with lithium by electroplating, electroless (chemical) plating, laser plating, sputtering, resistive thermal vapor deposition, electron beam vapor deposition, cluster ion beam vapor deposition, thermal CVD (chemical vapor deposition), vacuum CVD, plasma CVD, laser CVD, and the

like can be used. In addition, with a method, such as screen printing, an in or paste coating technique containing the metallic element not forming an alloy with lithium also may be used.

[0053] In another method a technique for using the base material comprising the metallic element not forming an alloy with lithium as the current collector as is and forming the layer comprising the metallic element forming an alloy with lithium thereon by a coating method, such as sputtering, resistive pressurization vapor deposition, electron beam vapor deposition, cluster ion beam vapor deposition, thermal CVD, vacuum CVD, plasma CVD and screen printing, also may be adopted. Various shapes, such as a plate, foil, punched metal, expanded metal, and mesh, can be used for the shape of the base material comprising the metallic element not forming an alloy with lithium.

[0054] <Metallic element forming an alloy with lithium and metallic element not forming an alloy with lithium> Aluminum, magnesium, potassium, sodium, calcium, strontium, barium, silicon, germanium, tin, lead, indium, zinc, and the like may be used for the metallic element forming an alloy with lithium, and aluminum, magnesium, calcium and lead are especially ideal. /8

[0055] Nickel, titanium, copper, silver, gold, platinum, iron, cobalt, chromium, tungsten, molybdenum, and the like can be used for the metallic element not forming an alloy with lithium, and nickel, titanium, copper, platinum and iron are especially ideal. An alloy comprising the above-mentioned elements can be adopted for the current collection member instead of a single metal of the above-mentioned element.

[0056] <Negative electrode comprising powder containing metallic element forming an alloy with lithium> A method for forming the negative electrode in which a resin or a low-melting point glass is mixed as the binder with a powder containing the metallic element forming an alloy with lithium or a powder of an alloy of a metallic element not forming an alloy with lithium, an organic solvent or the like is added, a paste whose viscosity was adjusted is coated on the current collection member of a metallic not forming an alloy with lithium, and subsequently dried or sintered may be adopted.

[0057] When an organic polymer is used as the above-mentioned binder, one that is stable in an electrolytic solution is preferable, and polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-propylene-diene terpolymer, a silicone resin, and the like may be cited as examples therefor. Other than these, a highly crosslinked polymer is cited as the preferred material. When the organic polymer is adopted for the binder, exfoliation of the active material due to expansion and contraction by charging/discharging is lessened, but the current collection ability is lower than in the case of a metal, and it is preferable to improve the current collection ability by adding a carbon powder, such as carbon black, kitchen black, acetylene black or graphite, or a fine metal powder, as the conduction adjuvant. In particular, if a flaky graphite having a bulk density of 0.1 or less is used in a thin form in a direction largely perpendicular to the horizontal direction in the crystal plane for the graphite used for the conduction adjuvant, the conductivity increases; hence, the current

collection ability is enhanced, and also, the amount of the electrolytic solution retained may be increased; hence, the impedance of the negative electrode formed from a powder can be reduced.

[0058] Although a low-melting point glass also can be used as the above-mentioned binder, in this case, the mechanical strength for expansion and contraction or bending is weaker than when a resin is used.

[0059] The above-mentioned current collection member must be a conductive material wherein at least the surface is covered with a metallic element not forming an alloy with lithium. Various shapes, such as platy, flaky, mesh-shaped, sponge-shaped, fibrous, punched metal, and expanded metal, may be adopted for the shape of the current collection member. Nickel, copper, titanium, aluminum, silver, gold, platinum, iron, stainless steel, and the like are cited for the material of the above-mentioned current collection member.

[0060] <Covering of current collection portion with conductor layer having high coefficient of extension> Methods, such as sputtering, resistive pressurized vapor deposition, electron beam vapor deposition, cluster ion beam vapor deposition, thermal CVD, vacuum CVD, plasma CVD, laser CVD, electroplating, electroless (chemical) plating, and laser plating, may be employed for specific methods for forming the conductor layer having a high coefficient of extension. In addition, a method for coating an ink containing a conductor having a high coefficient of extension, represented by screen printing, also can be used.

[0061] A conductor layer composed of at least one kind of conductor selected from tin, a tin-bismuth alloy, a tin-lead alloy, a zinc-aluminum

alloy, a copper-zinc alloy or a cadmium-zinc alloy, and a conductive ink bound by an organic polymer the conductor fine particles with an organic polymer material is cited as specific examples of the conductor layer having a high coefficient of extension arranged in the above-mentioned current collection portion of the negative electrode. In addition, as the case may be, gold, silver, aluminum and their alloys also may be used.

[0062] It is preferable that the organic polymer in the conductive ink used in the conductor layer having a high coefficient of extension of the negative electrode current collection portion above be a fluorine resin, polyolefin, silicone resin or highly-crosslinked polymer which does not react with the electrolytic solution. Furthermore, it is favorable that the glass transition temperature of the above-mentioned organic polymer be at most the lowest temperature of actual use temperatures. For example, it is preferably -30°C or less.

[0063] <Etching of negative electrode> By etching the surface of the negative electrode of the present invention composed of the member containing the metallic element forming an alloy with lithium and the current collection member comprising the metallic element not forming an alloy with lithium, the specific surface area of the negative electrode can be increased.

[0064] Techniques, such as chemical etching, electrochemical etching, and plasma etching, may be adopted for the etching method.

[0065] The chemical etching is an etching by reaction with an acid or alkali. The following compounds are included for specific examples.

[0066] Phosphoric acid, sulfuric acid, hydrochloric acid, nitric

acid, acetic acid, hydrofluoric acid, potassium hydroxide, sodium hydroxide, lithium hydroxide, mixed solutions of these, and the like are employed for the etchant for aluminum, which is the metallic element forming an alloy with lithium.

[0067] An aqueous alkali solution in which acetic acid, sulfuric acid, hydrochloric acid and an ammonium salt were mixed, a mixed solution of these, and the like are employed for the etchant when the metallic element forming an alloy with lithium is magnesium.

[0068] A dilute acid, such as nitric acid, can be used for the etchant when the metallic element not forming an alloy with lithium is nickel.

[0069] An organic acid, such as sulfuric acid, hydrochloric acid, nitric acid and acetic acid, and a cupric chloride solution, ferric chloride solution, aqueous ammonia, and the like may be used for the etchant when the metallic element not forming an alloy with lithium is copper. /9

[0070] Hydrofluoric acid, phosphoric acid, and the like can be used for the etchant when the metallic element not forming an alloy with lithium is titanium.

[0071] In the case of a chemical etching, the etching speed ratio of the metallic element forming an alloy with lithium and the metallic element not forming an alloy with lithium varies, and an etchant capable of selective etching is preferably used.

[0072] Electrochemical etching is conducted by applying an electric field across counter electrodes in the electrolytic solution and eluting this as metal ions electrochemically.

[0073] A mixed solution of phosphoric acid, sulfuric acid, and chromic

acid, and the like are used for the electrolytic solution of aluminum, which is a metallic element forming an alloy with lithium.

[0074] A phosphoric acid solution or the like can be used for the etchant when the metallic element not forming an alloy with lithium is copper.

[0075] The plasma etching is a method in which the gas for etching is made a plasma and etching is done by reacting reactive ions or radicals. Tetrachloromethane, tetrafluoromethane, chlorine, trichloromonofluoromethane, dichlorodifluoromethane, chlorotrifluoromethane, and the like may be used for the etching gas of the raw material.

[0076] <Covering surface of negative electrode> The effects for suppressing generation of dendrites during charging can be enhanced further by covering the lithium metal through which lithium ions selectively penetrate through the surface of the negative electrode of the cell of the present invention and deposits with an insulator film or semiconductor film through which the deposited lithium metal does not penetrate.

[0077] A material having a porous or molecular structure through which lithium ions can penetrate therethrough is used for the material covering the surface of the negative electrode of the present invention. Molecules having a large crown-like ether structure, calixarene (a wine cup-like cyclic compound comprising a plurality of phenol units), a molecular having a structure with ether bonds, and the like are cited as examples of a material having a molecular structure through which lithium ions can penetrate therethrough. Otherwise, a glassy substance or the like intercalated with lithium ions also can be used. A method in which a material

that can elute after forming a coating film of an electrolyte salt, is mixed with a solution of a coating material, a foaming agent, a material pyrolyzed easily, or the like is mixed therewith and fine porous are manufactured can be adopted for the method for manufacturing porous which allow lithium ions to penetrate therethrough actively.

[0078] <Input/output terminal of negative electrode> The input/output terminal of the negative electrode leads out from the current collection portion in which the metallic element not forming an alloy with lithium of the negative electrode is arranged. A technique for connecting the conductor member to the current collection portion by a method, such as laser welding, spot welding and soldering, is employed for leading out the terminal. In addition, when the negative electrode composed mainly of the metallic element forming an alloy with lithium is formed thereon using the base material comprising the metallic element not forming an alloy with lithium as the current collector, the leading out portion connected to the input/output terminal may be provided on the current collector by machining.

[0079] Lithium secondary cell

Positive electrode

The positive electrode is composed of the current collector, positive electrode-activating material, conduction adjuvant, binder, and the like, and it is manufactured by mixing the positive electrode-activating material, conduction adjuvant, binder, and the like and forming this on the current collector. A powdery or fibrous aluminum, copper, nickel, stainless steel, carbon powder, such as carbon black, ketchen black and acetylene black,

and carbon fibers can be used for the conduction adjuvant used in the positive electrode. A binder that is stable in the electrolytic solution is preferred, and polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-propylene diene terpolymer, and the like are cited as examples.

[0080] A duty of the current collector is to supply a current consumed efficiently by the electrode reaction during charging/discharging or collect the current generated. Therefore, a substance that is highly conductive and inactive against the cell reaction is favorable. Nickel, titanium, copper, aluminum, stainless steel, platinum, hafnium, gold, zinc, various alloys, and composite metals having at least two of the above-mentioned materials are cited as preferred substances. Shapes, such as plate, foil-shaped, mesh-shaped, sponge-shaped, fibrous, punched metal, and extended metal may be adopted for the shape of the current collector.

[0081] A transition metal oxide or transition metal sulfide is commonly used for the positive electrode-activating material. Sc, Y, lanthanoid, actinoid, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au, which are elements partially having a d- or f-shell, are used for the transition metal element of the transition metal oxide or transition metal sulfide. It is preferable to mainly use first transition series metals, Ti, V, Cr, Mn, Fe, Co, Ni and Cu.

[0082] It is more preferable to use a substance containing lithium in a transition metal oxide or transition metal sulfide for the above-mentioned positive electrode activating substance. By using the positive electrode comprising the positive electrode activating substance

containing lithium, the negative electrode containing lithium is not prepared in advance; hence, there is a merit because the cell manufacturing process can be simplified. A method in which lithium hydroxide or a lithium salt to prepare the transition metal oxide or transition metal sulfide can be used as a method for preparing the positive electrode activating substance containing lithium. There also is a method for preparing it in which a pyrolytic reaction readily arises, a lithium compound, such as lithium hydroxide, lithium nitrate or lithium carbonate, is mixed with the transition metal oxide or transition metal sulfide and heat treated for another method.

[0083] Separator

The separator has a role for preventing short-circuiting between /10 the negative electrode and the positive electrode. Moreover, there is a case in which it plays a role in maintaining the electrolytic solution. The separator has pores through which lithium ions can migrate, and it is necessary that it be insoluble and stable in an electrolytic solution; hence, glass or a nonwoven fabric material of polypropylene, polyethylene, fluorine resin, polyamide, and the like, or a material having a microporous structure can be used. In addition, a metal oxide film or a resin film in which a metal oxide is conjugated also may be used. When a metal oxide film having a multilayered structure is used in particular, there is an effect for preventing a short circuit where it is difficult for a dendrite to pass through. When a fluorine resin film, which is a nonflammable material, or a glass or metal oxide film is used, the safety can be increased more.

[0084] Electrolyte

In addition to being used as is, a solution in which an electrolyte has been dissolved in a solvent and an electrolyte immobilized by adding a gelling agent, such as a polymer, to a solution is used for the electrolyte. Generally, it is used by holding an electrolytic solution in which an electrolyte was dissolved in a solvent in a porous separator.

[0085] It is preferable that the conductivity of the electrolyte be as high as possible, and a conductivity at 25°C of 1×10^{-3} S/cm or higher is favorable, and 5×10^{-3} S/cm is more preferable.

[0086] A salt comprising an acid, such as H_2SO_4 , HCl , and HNO_3 , lithium ions (Li^+), a Lewis acid ions (BF_4^- , PF_6^- , ClO_4^- , $CF_3SO_3^-$, $BPPh^-$ (Ph: phenyl group)), and mixed salts of these can be used. Besides the above-mentioned support electrolyte, salts of cations, such as sodium ions, potassium ions and tetraalkyl ammonium ions, and Lewis acid ions can be used. It is favorable to heat the above-mentioned salts under reduced pressure to perform sufficient dehydration and deoxygenation.

[0087] Acetonitrile, benzonitrile, propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, dimethyl formamide, tetrahydrofuran, nitrobenzene, dichloroethane, dimethoxyethane, 1,2-dimethoxyethane, chlorobenzene, γ -butyrolactone, dioxolane, sulfolane, nitromethane, dimethylsulfide, dimethylsulfoxide, dimethoxyethane, methyl formate, 3-methyl-2-oxydazolidinone [translator's note: misspelled in source as 'okidazolidinone], 2-methyltetrahydrofuran, 3-propyl sydnone, sulfur dioxide, phosphoryl chloride, thionyl chloride, sulfuryl chloride, and the like, and mixtures of these may be used for the solvent of the electrolyte.

[0088] The above-mentioned solvent is dehydrated with active alumina, a molecular sieve, phosphorus pentaoxide and calcium chloride, or distilled with a solvent in the presence of an alkali metal in an inert gas, and impurities are removed and dehydration is performed.

[0089] To prevent leakage of the electrolytic solution, it is preferable to gel it. It is favorable to use a polymer so that it swells by absorbing the solvent of the electrolytic solution for the gelling agent. A polymer, such as polyethylene oxide, polyvinyl alcohol, or polyacrylamide, can be used.

[0090] Shape and structure of cell

The shape of an actual cell is not limited in particular and there are flat-shaped, cylindrical, right-angled parallelepiped, and sheet-shaped cells, etc. With a spiral cylindrical cell, the electrode area can be increased by sandwiching a separator between the negative electrode and the positive electrode, and a large current can be conducted during charging/discharging. In addition, with the right-angled parallelepiped cell, the space accommodating equipment accommodating the secondary cell can be effectively utilized. A structure such as a monolayer type or multilayered type can be used for the structure as well.

[0091] Figures 4 and 5 are examples of schematic cross sections of a monolayer-type flat cell and a spiral structure cylindrical cell. In Figures 4 and 5, 300 and 400 are negative electrode current collectors; 301 and 401 are negative electrode-activating materials; 303 and 403 are positive electrode-activating materials; 404 is a positive electrode current collector; 305 and 405 are negative electrode terminals (negative electrode

caps) ; 306 and 406 are positive electrode cans; 307 and 407 are an electrolyte and separator; 310 and 410 are insulating packings; and 411 is an insulating plate.

[0092] For an example of assembling the cells in Figures 4 and 5, the separators 307 and 407 are sandwiched by the are positive electrode-activating materials 303 and 403 formed with the negative electrode activating substance 301 and 401, an integrated electrolytic solution is charged into the positive electrode cans 306 and 406, after which the negative electrode terminals 305 and 405 and the insulation packings 310 and 410 are put together so as to manufacture a cell. Moreover, the negative electrode current collectors 300 and 400 in the drawings are connected to a metal not forming an alloy with the lithium of the negative electrode activating substance 301 and 401, as shown in Figures 2 and 3. In addition, depending on the case, the negative electrode current collectors 300 and 400 themselves may be metals not forming alloys with lithium.

[0093] Moreover, preparation of the material of the lithium cell and assembly of the cell are favorably performed in dry air or dry inert gas from which moisture was sufficiently removed.

[0094] Insulated packing

Fluorine resin, polyamide resin, polysulfone resin, and various rubbers can be used for the material of the insulation packings 310 and 410. For the sealing method, besides caulking using a gasket, such as an insulating packing, as shown in Figures 4 and 5, methods, such as glass tube sealing, an adhesive, welding and soldering, may be used ideally.

[0095] In addition, various organic resin materials and ceramics may be used ideally as the material of the insulating plate 411 in Figure 5.

[0096] Outer can
Stainless steel, and in particular, a titanium-clad stainless steel, copper-clad stainless steel, nickel-plated steel plate, and the like may be used ideally for the materials of the positive electrode cans 306 /11 and 406 and the negative electrode terminals 305 and 405.

[0097] Although the positive electrode cans 306 and 406 served as cell cases in Figures 4 and 5, besides stainless steel, a metal such as zinc, a plastic, such as polypropylene, a composite material of a metal, glass fibers and plastic may be used for the material of the cell case.

[0098] Safety valve
Although not illustrated in Figures 4 and 5, it is preferable that a safety valve, such as a rubber, spring, metal pole or rupture foil be provided for the safety measure when the internal pressure of the cell increases.

[0099]

[Practical Examples] The present invention will now be described in detail based on the practical examples. Moreover, the present invention is not limited to these practical examples.

[0100] (Practical Example 1) A lithium secondary cell having the schematic cross-section structure shown in Figure 4 for which the structure and assembly were simple was manufactured. A 50%-50% titanium-aluminum alloy foil polished to a thickness of 50 microns was immersed for 5 minutes in a 5% by weight aqueous potassium hydroxide solution to etching aluminum

on the surface, after which it was washed with water and dried, and used as the negative electrode 301 (titanium is the metal element which does not form an alloy with lithium). Moreover, the surface roughness of the surface of the negative electrode facing the positive electrode was measured in a tracer method by a surface polishing and etching treatment of the titanium-aluminum alloy plate before manufacturing the above-mentioned negative electrode was so adjusted that the centerline average roughness was at most 0.6 microns and the maximum height was at most 3.8 microns. At this time, with respect to a measured length of 80 microns, there were seven 7 peaks of roughness.

[0101] Electrolytic manganese dioxide and lithium carbonate were mixed at a 1:0.4 ratio for the positive electrode-activating material, subsequently dried at 800°C and a lithium-manganese oxide was prepared. 3% by weight of a carbon powder of acetylene black and 5% by weight of a polyvinylidene fluoride powder were mixed with the prepared lithium-manganese oxide, N-methyl-2-pyrrolidone was added and prepared like a paste, after which it was coated and dried on aluminum foil to form the positive electrode.

[0102] An electrolytic solution in which 1M (mol/L) of a lithium tetrafluoroborate was dissolved in an equal amount of a mixed solvent of ethylene carbonate (EC) and dimethoxycarbonate (DMC) with the moisture removed sufficiently was used as the electrolytic solution.

[0103] A separator prepared to a thickness of 50 microns by sandwiching it between a polypropylene nonwoven fabric and a porous film was used as the separator.

[0104] Assembly was performed in a dry argon gas atmosphere, the separator was sandwiched between the negative electrode and positive electrode inserted into a titanium-clad stainless steel positive electrode, charged with the electrolytic solution, subsequently sealed with a titanium-clad stainless steel negative electrode cap and a fluorine rubber insulation packing, and a lithium secondary cell was manufactured.

[0105] (Practical Example 2) A lithium secondary cell having the schematic cross-sectional structure shown in Figure 4 for which the structure and assembly were simple was manufactured.

[0106] The negative electrode was manufactured first according to the following procedure. A 30 micron thick aluminum foil was immersed for 5 minutes in a 5% aqueous potassium hydroxide solution to etch the surface, and subsequently washed and dried. Next, it was immersed for 5 minutes in a 50°C 20% by weight aqueous nickel chloride solution, a portion of the aluminum on both sides was substituted with nickel, subsequently washed with water and vacuum-dried at 150°C (nickel is a metallic element not forming an alloy with lithium). Moreover, the surface roughness of the surface of the negative electrode facing the positive electrode measured in a tracer method was so adjusted that the centerline average roughness was at most 0.4 microns and the maximum height was at most 2.0 microns. At this time, with respect to a measured length of 80 microns, there were eight 8 peaks of roughness.

[0107] A 25 micron thick polypropylene porous film was used for the separator.

[0108] A cell was assembled hereafter as in Practical Example 1.

[0109] (Practical Example 3) A lithium secondary cell having the schematic cross-sectional structure shown in Figure 6 for which the structure and assembly were simple was manufactured.

[0110] A negative electrode was manufactured by forming a conductive ink obtained by dispersing a fine powder of silver in a -30°C glass transition temperature epoxy resin in an epoxy resin to a thickness of 10 microns on the surface of the current collection side of the negative electrode manufactured by the same operation in Practical Example 2, and crosslinking and curing this at 150°C under reduced pressure to form a conductive layer.

[0111] A cell was assembled hereafter as in Practical Example 1.

[0112] (Practical Example 4) A lithium secondary cell having the schematic cross-sectional structure shown in Figure 4 for which the structure and assembly were simple was manufactured.

[0113] A negative electrode was manufactured first according to the following procedure. A 30 micron thick aluminum foil was immersed in a 5% aqueous hydrofluoric acid solution to etch the surface, and subsequently washed and dried. Next, a 50 nanometer thick copper plating was conducted on both sides in a mixed aqueous solution of copper sulfate and sulfuric acid, vacuum-dried at 150°C, and a tin-bismuth alloy was subsequently formed to 500 nanometers on the surface on the current collection side to manufacture a negative electrode (copper is the metallic element not forming an alloy with lithium and the tin-bismuth alloy is the alloy forming a conductor having a high coefficient of extension). Moreover, by a surface polishing and an etching treatment, the surface roughness of the surface of the negative electrode facing the positive electrode measured in a

tracer method was so adjusted that the centerline average roughness was at most 0.3 microns and the maximum height was at most 1.7 microns. At this time, with respect to a measured length of 80 microns, there were eight 8 peaks of roughness.

[0114] A cell was assembled hereafter as in Practical Example 1.

[0115] (Practical Example 5) A lithium secondary cell having the schematic cross-sectional structure shown in Figure 4 for which the structure and assembly were simple was manufactured.

[0116] A negative electrode was manufactured first according to the following procedure. A 300-mesh aluminum powder, polyvinylidene fluoride powder, for the binder, acetylene black and flaky graphite were mixed at a weight ratio of 89:5:3:3, N-methyl-2-pyrrolidone was added to /12 prepare a paste, which was coated on a 35 micron tin-plated steel foil, the coated thickness was adjusted uniformly with a roll press machine, and vacuum-dried at 150°C to manufacture a 70 micron negative electrode.

[0117] A cell was assembled hereafter as in Practical Example 1.

[0118] (Practical Example 6) A lithium secondary cell having the schematic cross-sectional structure shown in Figure 4 for which the structure and assembly were simple was manufactured.

[0119] A negative electrode was manufactured first according to the following procedure. A 300-mesh aluminum powder, superfine nickel powder having a particle size of at most 0.1 microns, and methyl cellulose, for the binder, were mixed at a weight ratio of 90:5:5 with a nickel-plated iron punched metal foil, xylene was added and made like a paste, then coated on a 35 micron thick nickel foil, the coated thickness was adjusted

uniformly with a roll press machine and dried at 100°C. Next, this was sintered under reduced pressure at 700°C.

[0120] Next, this was dipped for 5 minutes at 50°C in a 20% by weight aqueous nickel chloride solution, a portion of the aluminum of the aluminum powder was substituted with nickel, washed and dried, and subsequently vacuum-dried at 150°C to manufacture a 60 micron thick negative electrode.

[0121] A cell was assembled hereafter as in Practical Example 1.

[0122] (Practical Example 7) A lithium secondary cell having the schematic cross-sectional structure shown in Figure 4 for which the structure and assembly were simple was manufactured.

[0123] A negative electrode was manufactured first according to the following procedure. A 250-mesh 40%-60% nickel-aluminum alloy powder and methyl cellulose for the binder were mixed at a weight ratio of 90:10, xylene was added and prepared like a paste, coated on a 35 micron thick nickel expanded metal foil with a coater, the coated thickness was adjusted uniformly with a roll press machine, and dried at 100°C. This was sintered next under a reduced pressure at 700°C. This was dipped for 5 minutes in a 5% by weight aqueous potassium hydroxide solution next to etch the surface and prepare a 50 micron thick negative electrode.

[0124] A cell was assembled hereafter as in Practical Example 1.

[0125] (Practical Example 8) A lithium secondary cell having the schematic cross-sectional structure shown in Figure 4 for which the structure and assembly were simple was manufactured.

[0126] A negative electrode was manufactured first according to the following procedure. A 300 mesh 50%-50% lithium-aluminum alloy powder,

150-mesh magnesium powder and acetyl cellulose, as the binder, were mixed at a weight ratio of 45:45:10, xylene was added and prepared like a paste, coated on a 35 micron thick nickel expanded metal foil with a coater, the coated thickness was adjusted uniformly with a roll press machine and dried at 100°C. This was sintered next under reduced pressure at 700°C. This was dipped for 5 minutes in a 5% by weight aqueous potassium hydroxide solution next to etch the surface and a 60 micron thick negative electrode was manufactured.

[0127] A cell was assembled hereafter as in Practical Example 1.

[0128] (Practical Example 9) A lithium secondary cell having the schematic cross-sectional structure shown in Figure 4 for which the structure and assembly were simple was manufactured.

[0129] First of all, a xylene solution of a copolymer of a tetrafluoroethylene and vinyl ether made by Nippon Oils & Fats Co. Ltd. (trade name: Super Konac F) and a lithium borofluoride dimethyl carbonate solution were mixed to prepare a solution for covering the surface. Moreover, 1% by weight of lithium borofluoride was mixed with the entire mixed solution. Next, the solution for covering the surface prepared previously was coated using a spinner on the surface of a negative electrode manufactured by the same operation as in Practical Example 4 facing the positive electrode, dried and cured under reduced pressure at 170°C, then irradiated with UV radiation, and a negative electrode whose surface was covered with a lithium ion-penetrable film to a film thickness of about 100 nanometers.

[0130] A cell was assembled hereafter as in Practical Example 1.

[0131] Moreover, a lithium-manganese oxide type is used to evaluate

the performance of the negative electrode in the positive electrode-activating materials of Practical Examples 1 to 9 above, but the present invention is not limited thereto, and various positive electrode-activating materials, such as lithium-nickel oxide and lithium-cobalt oxide also may be adopted.

[0132] In addition, although the same electrolytic solution was used in Practical Examples 1 to 9, the present invention is not limited thereto.

[0133] (Comparative Example 1) A cell having the schematic cross-sectional structure shown in Figure 4, as in the practical examples, was manufactured according to the same procedure as in Practical Example 1 using a 30 micron thick aluminum foil in place of the negative electrode in Practical Example 1. Moreover, the surface roughness of the surface of the negative electrode facing the positive electrode measured in a tracer method was so adjusted that the centerline average roughness was at most 0.15 micron and the maximum height was at most 0.7 micron. At this time, with respect to a measured length of 80 microns, there were six 6 peaks of roughness.

[0134] (Comparative Example 2) A cell having the schematic cross-sectional structure shown in Figure 4, as in the practical examples, was manufactured according to the same procedure as in Practical Example 1 using a 100 micron thick aluminum foil whose surface was etched (made by Japan Capacitor Industrial Co., Ltd.) in place of the negative electrode in Practical Example 1.

[0135] (Comparative Example 3) A cell having the schematic cross-sectional structure shown in Figure 4, as in the practical examples,

was manufactured according to the same procedure as in Practical Example 2 using a graphite negative electrode manufactured according to the procedure below in place of the negative electrode in Practical Example 2. A natural graphite powder was heat treated at 2,000°C for the graphite negative electrode, a natural graphite powder, acetylene black, and polyvinylidene fluoride powder were mixed at a weight ratio of 82:3:5, N-methyl-2-pyrrolidone was added to prepare it like a paste, after which this was coated on a 35 micron thick copper foil, the coated thickness was adjusted uniformly with a roll press machine, and vacuum-dried at 150°C to manufacture a 110 micron thick negative electrode.

[0136] Performance evaluation of lithium secondary cell

A charging/discharging cycle test was performed at the conditions /13 below to evaluate the performance of the lithium secondary cells manufactured in the practical examples and comparative examples, and the performance was evaluated as compared with the cells of the comparative examples.

[0137] The cycle test conditions included a charging/discharging [current] of 0.5 C (current 0.5 times the capacity/time), a charging cutoff voltage of 4.5 V, a rest time of 30 minutes, and a discharging cutoff voltage of 2.5 V, based on the electrical capacity calculated from the amount of positive electrode-activating material. The charging was so determined that decomposition of the solvent in the electrolytic solution did not proceed. A HJ-106 M, made by Hokuto Denko Corp., was used for the cell charging/discharging device. Moreover, the charging/discharging test was started after a charging, and the cell capacity was defined as the amount of the 3rd discharge while the cycle life was defined as the

cycle frequency reaching a charging potential of 4.5 V.

[0138] The results upon evaluating the performance in relation to the discharge energy density and cycle life per unit area of the lithium cells manufactured using the negative electrode of the present invention, e.g., the cells of the practical examples and the comparative examples were shown collectively in Table 1, with the performance of the cell of the Comparative Example 1 standardized as 1.0.

[0139] As can be understood from Table 1, it was seen from a comparison between Practical Examples 1 to 9 and Comparative Examples 1 and 2, that the secondary cells using the negative electrode of the present invention were adopted, the surface of the negative electrode was activated and the current collection ability was improved, whereby the cycle life was extended. Moreover, it was seen from a comparison between Practical Examples 1 to 9 and Comparative Example 3 that secondary cells having a high energy density could be manufactured although the life was substantially the same as a carbon negative electrode.

[0140]

[Table 1]

Table 1

	エネルギー密度	サイクル寿命
実施例1の二次電池	1.4	2.9
実施例2の二次電池	1.6	3.2
実施例3の二次電池	1.6	3.7
実施例4の二次電池	1.8	3.5
実施例5の二次電池	1.3	3.3
実施例6の二次電池	1.4	3.0
実施例7の二次電池	1.4	3.4
実施例8の二次電池	1.4	3.0
実施例9の二次電池	1.6	3.9
比較例1の二次電池	1.0	1.0
比較例2の二次電池	1.1	1.3
比較例3の二次電池	1.0	4.2

Key:

	Energy Density	Cycle Life
Secondary cell of Practical Example 1		
Secondary cell of Practical Example 2		
Secondary cell of Practical Example 3		
Secondary cell of Practical Example 4		
Secondary cell of Practical Example 5		
Secondary cell of Practical Example 6		
Secondary cell of Practical Example 7		
Secondary cell of Practical Example 8		
Secondary cell of Practical Example 9		
Secondary cell of Comparative Example 1		
Secondary cell of Comparative Example 2		
Secondary cell of Comparative Example 3		

[0141]

[Advantages of the Invention] A lithium secondary cell having a long charging/discharging cycle life and high energy density can be provided according to the present invention described above.

[0142] In addition, according to the present invention, an electrode for a cell having a negative electrode structure capable of checking a reduction in the current collection ability due to fine powdering and generation of fissures owing to deposition and dissolution of lithium during charging/discharging and a lithium secondary cell having the electrode can be provided.

[Brief Description of the Drawings]

[Figure 1] A conceptual schematic diagram for describing a preferred embodiment of the secondary cell of the present invention.

[Figure 2] (a), (b), (c) and (c') are schematic cross sections showing a preferred embodiment of the negative electrode of the present invention, respectively.

[Figure 3] (d), (e), (f) and (g) are schematic cross sections showing a preferred embodiment of the negative electrode of the present invention,

respectively.

[Figure 4] A schematic cross section for describing an example of a monolayer flat cell.

[Figure 5] A schematic cross section for describing an example of a spiral cylindrical cell.

[Figure 6] A drawing for describing an example of the results of measuring the surface of the negative electrode in a tracer method.

[Figure 7] A drawing showing an example of the relationship between one-half of the maximum height of the roughness R_{max} of a conductor portion of the surface of the negative electrode, and the centerline average roughness R_a .

[Figure 8] A drawing showing an example of the relationship between the centerline average roughness R_a of the conductor portion on the surface of the negative electrode, the measured length L , the number n of peaks per measured length L , and the cycle life of the negative electrode.

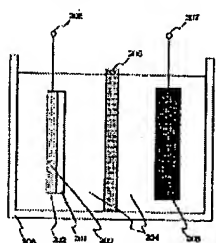
[Explanation of the Codes]

101: current-collecting portion comprising the metallic element not forming an alloy with lithium; 102: member containing the metallic element forming an alloy with lithium; 103: powdery member containing the metallic element forming an alloy with lithium; 104: conduction adjuvant; 105: binder; 106: metallic element not forming an alloy with lithium; 107: conductor layer having high coefficient of extension; 108: alloy of the metallic element forming an alloy with lithium and the metallic element not forming an alloy with lithium; 200: current collection portion; 201: layer comprising member containing metallic element forming an alloy

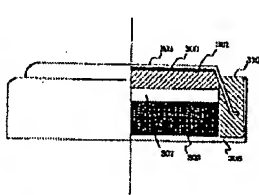
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with lithium; 202: negative electrode; 203: positive electrode; 204: electrolyte (electrolytic solution); 205: separator; 206: negative electrode terminal; 207: positive electrode terminal; 208: cell case; 300: negative electrode current collector; 301: negative electrode-activating material (or negative electrode); 303: positive electrode-activating material (or positive electrode); 305: negative electrode terminal; 306: positive electrode can; 307: electrolyte and separator; 310: insulation packing; 400: negative electrode current collector; 401: negative electrode-activating material (or negative electrode); 403: positive electrode-activating material (or positive electrode); 404: positive electrode current collector; 405: negative electrode terminal; 406: positive electrode can; 407: electrolyte and separator; 410: insulation packing; 411: insulation plate

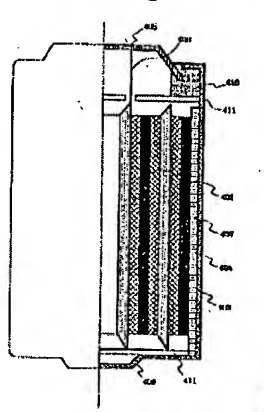
[Figure 1]



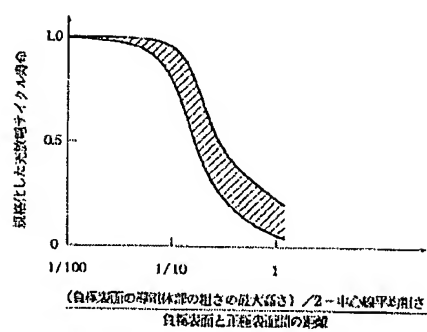
[Figure 4]



[Figure 5]

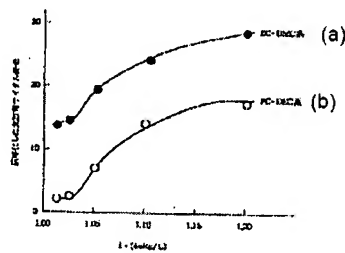


[Figure 7]



Key: x-axis) ((Maximum Height of Roughness of Conductor Portion on Negative Electrode Surface)/2-Centerline Average Roughness)/(Distance Between Negative Electrode surface and Positive Electrode Surface); Y-axis) Standardized Charging/Discharging Cycle Life

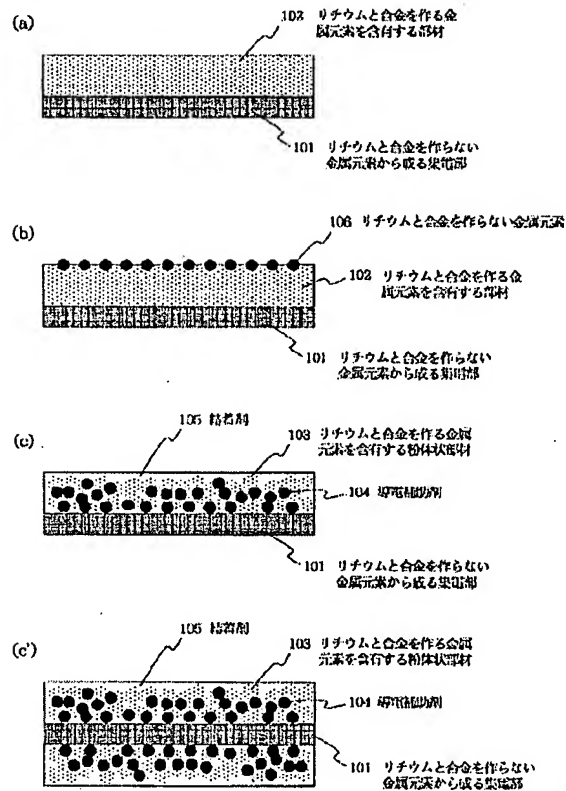
[Figure 8]



Key: a) EC-DMC-based; b) PC-DEC-based; Y-axis) Standardized Charging/Discharging Cycle Life

[Figure 2]

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Key (a): 102) member containing the metallic element forming an alloy with lithium; 101) current-collecting portion comprising the metallic element not forming an alloy with lithium

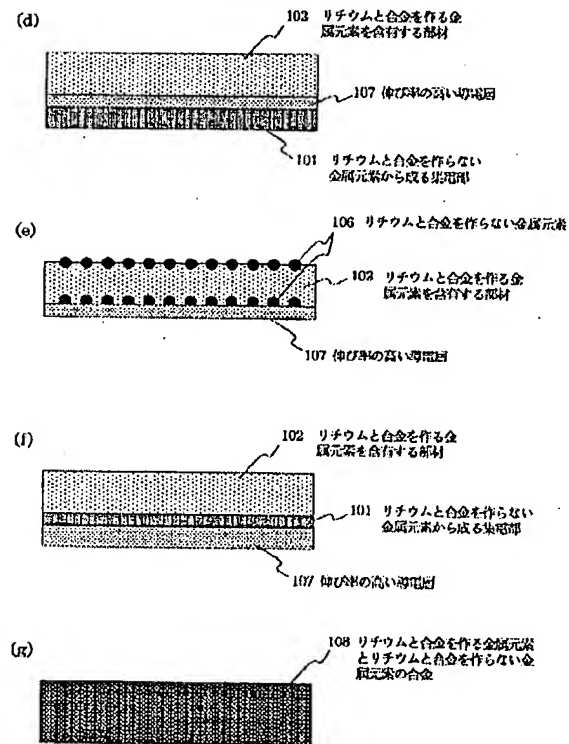
Key (b): 106) metallic element not forming an alloy with lithium; 102) member containing the metallic element forming an alloy with lithium; 101) current-collecting portion comprising the metallic element not forming an alloy with lithium

Key (c): 105) binder; 103) powdery member containing the metallic element forming an alloy with lithium; 104) conduction adjuvant; 101) current-collecting portion comprising the metallic element not forming an alloy with lithium

Key (d): 105) binder; 103) powdery member containing the metallic element forming an alloy with lithium; 104) conduction adjuvant; 101) current-collecting portion comprising the metallic element not forming an alloy with lithium

[Figure 3]

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Key (d): 102) member containing the metallic element forming an alloy with lithium; 107) conductor layer having high coefficient of extension; 101) current-collecting portion comprising the metallic element not forming an alloy with lithium

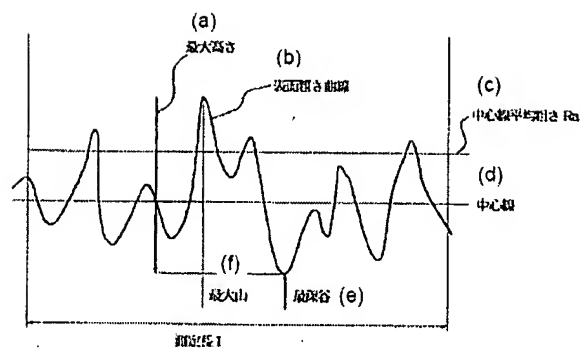
Key (e): 106) metallic element not forming an alloy with lithium; 102) member containing the metallic element forming an alloy with lithium; 107) conductor layer having high coefficient of extension

Key (f): 102) member containing the metallic element forming an alloy with lithium; 101) current-collecting portion comprising the metallic element not forming an alloy with lithium; 107) conductor layer having high coefficient of extension

Key (g): 108) alloy of the metallic element forming an alloy with lithium and the metallic element not forming an alloy with lithium

[Figure 6]

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Key: a) maximum height; b) surface roughness curve; c) centerline average roughness Ra; d) centerline; e) highest peak; f) deepest valley; X-axis) Measured Length l